

of the aqueous solution of ammonium perrhenate (manufactured by Mitsuwa Chemicals Co. Ltd.) was changed, a catalyst for the water gas shift reaction was obtained wherein the zirconia carrier supported 3.0 % by weight of platinum and 3.0 % by weight of rhenium.

As to the prepared catalysts of Examples 17 and 18 and Example 3 and Comparative Example, the CO removing experiments were carried out similarly to the above. The results are shown in Fig. 4. It is seen from Fig. 4 that the catalysts of Examples 17 and 18 have high activities, and they are highly active even at a temperature equal to or lower than 250 °C.

Example 19

A predetermined amount of the zirconia carrier which was prepared in Examples 1 to 5 was charged into an evaporating dish located above a water bath. An appropriate amount of pure water was added to the carrier and they are mixed intimately. An aqueous solution of chloroplatinic acid (manufactured by NACALAI TESQUE INC.) was added to the evaporating dish, and pure water was further added to reach a predetermined concentration. The dish was located above the water bath while stirring so that evaporation to dryness of the contents in the dish was

carried out for one hour, during which a metal salt depositing on a wall of the evaporating dish were washed away with pure water into the bottom of the dish. Such depositing salt arose with proceeding of the water evaporation. The obtained material through the evaporation to dryness was dried dry at a temperature of about 100 °C for at least 15 hours.

The catalyst thus obtained was stirred in hot water (at a temperature of about 100 °C) for about one hour followed by settling and filtrating the catalyst. This process was repeated until the filtrate became clear. Then, the filtrated catalyst was dried at a temperature of 100 °C for at least 15 hours.

Then, thus obtained catalyst was pressed at a pressure of about 3600 kg/cm² for about 10 seconds using a manually operated press, and obtained pellets were pulverized into particles of which diameter was in the range between 0.5 mm and 1.0 mm, whereby a catalyst for the water gas shift reaction was obtained which supported platinum of 3.0 % by weight on the zirconia carrier.

As to the prepared catalyst of Examples 19, the same activity aging experiment was carried out similarly to the experiments as to the catalysts of Examples 3 and 4 and Comparative Example. The results are shown in Fig. 5. It

is seen from Fig. 5 that the catalyst of Example 19 has a further higher activity than of course the catalyst of Comparative Example or the catalyst of Example 3 or 4, and that similarly to the catalysts of Examples 3 and 4, the activity of the catalyst of Example 19 does not degrade.

Examples 20 to 27

Using a firing furnace, an agent shown in Table 4 below was subjected to a firing treatment wherein it was heated to a temperature of 500 °C in one hour in an air flow of 60 ml/min., and kept at that temperature for one hour, and thereby a carrier of each of Examples 20 to 27 was prepared.

A predetermined amount of the obtained each carrier was charged into an evaporating dish located above a water bath. Pure water was added to the carrier and they are mixed intimately. An aqueous solution of chloroplatinic acid hexahydrate (manufactured by NACALAI TESQUE INC.) was added to the evaporating dish, and pure water was further added to reach a predetermined concentration. The dish was located above the water bath while stirring so that the evaporation to dryness of the contents in the dish was carried out, during which a metal salt depositing on a wall of the evaporating dish was washed away with pure water into the bottom of the dish. Such depositing salt arose with

the water evaporation. The evaporation to dryness took two hours.

The obtained material through the evaporation to dryness was further dried at a temperature about 100 °C for at least 15 hours. The dried material was pulverized into powder in an agate mortar, and the powder was subjected to a firing treatment wherein it was heated to a temperature of 500 °C in one hour in an air flow of 60 ml/min., and kept at that temperature for one hour.

Then, thus obtained powder was pressed at a pressure of about 3600 kg/cm² for 10 seconds using a manually operated press, and obtained pellets were pulverized into particles of which diameter was in the range between 1.4 mm and 2.0 mm, whereby a catalyst for the water gas shift reaction was obtained. The catalyst of each Example supported 3 % by weight of platinum.

Table 4

| Example | feedstock for carrier | manufacturer |
|------------|-----------------------|---|
| Example 20 | alumina | NACALAI TESQUE INC. |
| Example 21 | titania | reference catalyst of Catalysis Society |
| Example 22 | silica | Davison Inc. |
| Example 23 | magnesia | KANTO KAGAKU |
| Example 24 | niobium oxide | NACALAI TESQUE INC. |

| | | |
|------------|----------------|--|
| Example 25 | zinc oxide | NACALAI TESQUE INC. |
| Example 26 | chromium oxide | NACALAI TESQUE INC. |
| Example 27 | zeolite | reference catalyst of Catalysis Society |

As to the catalysts for the water gas shift reaction of Example 3 and 20 to 27, the CO removal performances were estimated. The estimation experiments were carried out as follows:

First, 3.3 ml of the catalyst for the water gas shift reaction was charged in to a reaction tube, and H₂O and a gas mixture which contained H₂ (70 %), CO (10 %), CO₂ (15 %) and CH₄ (5 %) were supplied to the tube under conditions of a molar ratio (H₂O/CO) of 7.5 and SV (based on the gas mixture) of 5000 (1/hr). The reaction for the CO removal started at a temperature of 250 °C.

After the reaction got stable, a sample was obtained from an outlet of the reaction tube, and analyzed using gas chromatography (thermal conductivity detector and flame ionization detector), whereby the conversion of CO to CO₂ was obtained.

The results are shown in Fig. 6. It is seen from Fig. 6 that the activity of the catalyst of each Example is higher than that of the Cu/ZnO catalyst of Comparative Example.

Example 28

Using the catalyst for the water gas shift reaction according to Example 17, the CO removing performance from a hydrogen gas which contained carbon monoxide was estimated. Experiments for the evaluation were carried out similarly to those as to the catalysts of Examples 20 to 27. It is noted that the similar CO removal experiments were carried out using the Cu/ZnO catalyst as Comparative Example.

The results are shown in Fig. 7. It is seen from Fig. 7 that the CO removal of Example 28 shows a further higher CO removal compared with the Comparative Example.

Example 29

A reformed gas rich in hydrogen which was produced from a butane gas as a hydrocarbon based fuel and steam through the steam reforming reaction was contacted with the catalyst for the water gas shift reaction according to Example 17, and then contacted with an Ru-based selective oxidation catalyst, and thus obtained reformed gas was supplied to a polymer electrolyte fuel cell. An amount of the reformed gas supplied to the fuel cell was 11.6 liters/min. according to an integrating flowmeter, and electricity generation of the fuel cell was estimated using

an electronically loading device (electronic load device).

Generation performance of the fuel cell is shown in the following table:

| current | voltage | electric power generation |
|------------|------------|---------------------------|
| 20 amperes | 16.8 volts | 336 watts |

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As seen from the above table, it is confirmed that in the fuel cell system of Example 29 the electricity generation is possible by means of the fuel cell using the reformed gas obtained by the steam reforming reaction of the fuel and through the water gas shift reaction and the selective oxidation reaction.

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